Rapid and Facile Synthesis of $(Zn_xAg_yIn_z)S_2$ Nanocrystal Library via Sono-Combichem Method and Its Characterization including Single Nanocrystal Analysis

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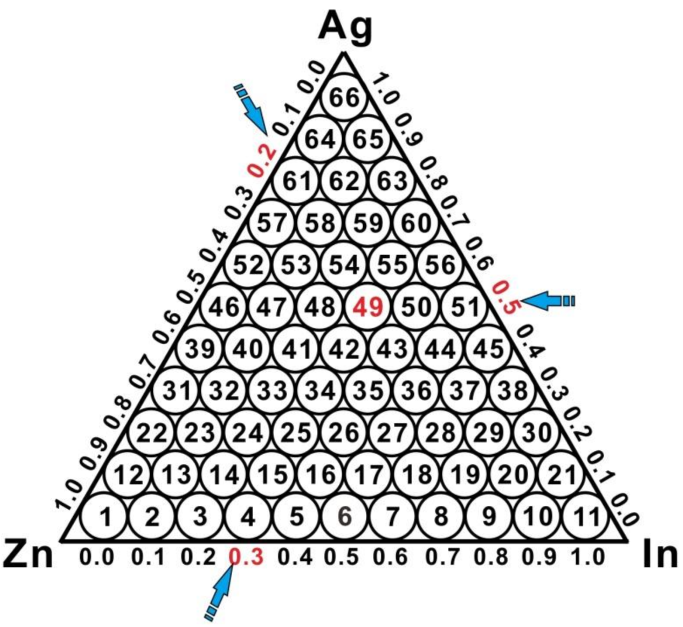

tZAIS 49 = $(Zn_{0.3}Ag_{0.2}In_{0.5})S_2$

1	$(Zn_0Ag_1In_0)S_2$	23	$(Zn_{0.1}Ag_{0.7}In_{0.2})S_2$	45	$(Zn_{0.6}Ag_0In_{0.4})S_2$
2	$(Zn_{0.1}Ag_{0.9}In_0)S_2$	24	$(Zn_{0.2}Ag_{0.6}In_{0.2})S_2$	46	$(Zn_0Ag_{0.5}In_{0.5})S_2$
3	$(Zn_{0.2}Ag_{0.8}In_0)S_2$	25	$(Zn_{0.3}Ag_{0.5}In_{0.2})S_2$	47	$(Zn_{0.1}Ag_{0.4}In_{0.5})S_2$
4	$(Zn_{0.3}Ag_{0.7}In_0)S_2$	26	$(Zn_{0.4}Ag_{0.4}In_{0.2})S_2$	48	$(Zn_{0.2}Ag_{0.3}In_{0.5})S_2$
5	$(Zn_{0.4}Ag_{0.6}In_0)S_2$	27	$(Zn_{0.5}Ag_{0.3}In_{0.2})S_2$	49	$(Zn_{0.3}Ag_{0.2}In_{0.5})S_2$
6	$(Zn_{0.5}Ag_{0.5}In_0)S_2$	28	$(Zn_{0.6}Ag_{0.2}In_{0.2})S_2$	50	$(Zn_{0.4}Ag_{0.1}In_{0.5})S_2$
7	$(Zn_{0.6}Ag_{0.4}In_0)S_2$	29	$(Zn_{0.7}Ag_{0.1}In_{0.2})S_2$	51	$(Zn_{0.5}Ag_0In_{0.5})S_2$
8	$(Zn_{0.7}Ag_{0.3}In_0)S_2$	30	$(Zn_{0.8}Ag_0In_{0.2})S_2$	52	$(Zn_0Ag_{0.4}In_{0.6})S_2$
9	$(Zn_{0.8}Ag_{0.2}In_0)S_2$	31	$(Zn_0Ag_{0.7}In_{0.3})S_2$	53	$(Zn_{0.1}Ag_{0.3}In_{0.6})S_2$
10	$(Zn_{0.9}Ag_{0.1}In_0)S_2$	32	$(Zn_{0.1}Ag_{0.6}In_{0.3})S_2$	54	$(Zn_{0.2}Ag_{0.2}In_{0.6})S_2$
11	$(Zn_1Ag_0In_0)S_2$	33	$(Zn_{0.2}Ag_{0.5}In_{0.3})S_2$	55	$(Zn_{0.3}Ag_{0.1}In_{0.6})S_2$
12	$(Zn_0Ag_{0.9}In_{0.1})S_2$	34	$(Zn_{0.3}Ag_{0.4}In_{0.3})S_2$	56	$(Zn_{0.4}Ag_0In_{0.6})S_2$
13	$(Zn_{0.1}Ag_{0.8}In_{0.1})S_2$	35	$(Zn_{0.4}Ag_{0.3}In_{0.3})S_2$	57	$(Zn_0Ag_{0.3}In_{0.7})S_2$
14	$(Zn_{0.2}Ag_{0.7}In_{0.1})S_2$	36	$(Zn_{0.5}Ag_{0.2}In_{0.3})S_2$	58	$(Zn_{0.1}Ag_{0.2}In_{0.7})S_2$
15	$(Zn_{0.3}Ag_{0.6}In_{0.1})S_2$	37	$(Zn_{0.6}Ag_{0.1}In_{0.3})S_2$	59	$(Zn_{0.2}Ag_{0.1}In_{0.7})S_2$
16	$(Zn_{0.4}Ag_{0.5}In_{0.1})S_2$	38	$(Zn_{0.7}Ag_0In_{0.3})S_2$	60	$(Zn_{0.3}Ag_0In_{0.7})S_2$
17	$(Zn_{0.5}Ag_{0.4}In_{0.1})S_2$	39	$(Zn_0Ag_{0.6}In_{0.4})S_2$	61	$(Zn_0Ag_{0.2}In_{0.8})S_2$
18	$(Zn_{0.6}Ag_{0.3}In_{0.1})S_2$	40	$(Zn_{0.1}Ag_{0.5}In_{0.4})S_2$	62	$(Zn_{0.1}Ag_{0.1}In_{0.8})S_2$
19	$(Zn_{0.7}Ag_{0.2}In_{0.1})S_2$	41	$(Zn_{0.2}Ag_{0.4}In_{0.4})S_2$	63	$(Zn_{0.2}Ag_0In_{0.8})S_2$
20	$(Zn_{0.8}Ag_{0.1}In_{0.1})S_2$	42	$(Zn_{0.3}Ag_{0.3}In_{0.4})S_2$	64	$(Zn_0Ag_{0.1}In_{0.9})S_2$
21	$(Zn_{0.9}Ag_0In_{0.1})S_2$	43	$(Zn_{0.4}Ag_{0.2}In_{0.4})S_2$	65	$(Zn_{0.1}Ag_0In_{0.9})S_2$
22	$(Zn_0Ag_{0.8}In_{0.2})S_2$	44	$(Zn_{0.5}Ag_{0.1}In_{0.4})S_2$	66	$(Zn_0Ag_0In_1)S_2$

Fig. S1 Total compositional ternary library of $(Zn_xAg_yIn_z)S_2$ (tZAIS) NCs in terms of Zn, Ag, and In metal ratios. tZAIS 49 is an example of the numbering system.

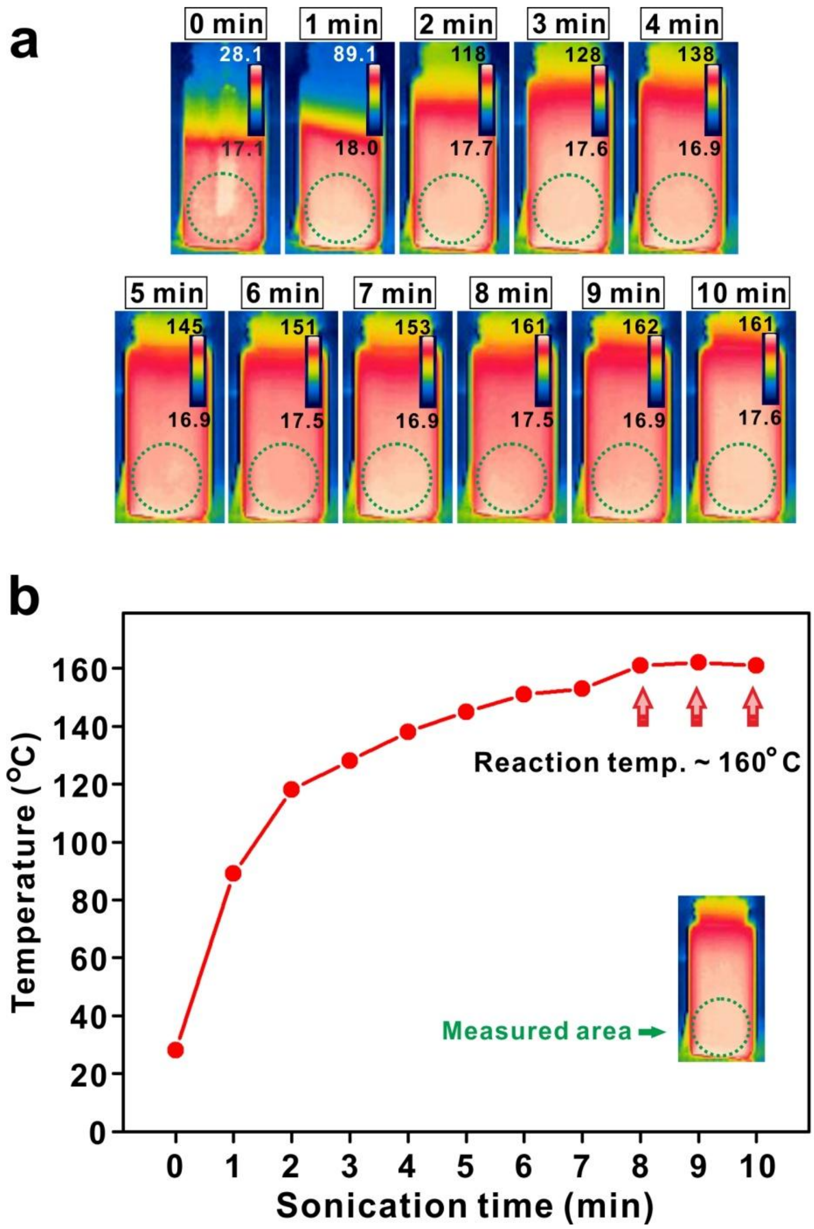

Fig. S2 Sonochemical synthesis of $(Zn_xAg_yIn_z)S_2$ NCs. **(a)** Thermal images of the reaction vial taken by an infrared camera (FLIR T200, Sweden) for the synthesis of $(Zn_xAg_yIn_z)S_2$ NCs. Sonication in the vial increases temperature of the reaction solution up to about 160 °C. The ultrasonic irradiation time usually takes 10 min for the synthesis of $(Zn_xAg_yIn_z)S_2$ NCs. **(b)** Temperatures of the local hot spot are plotted. Measured area (inset) is shown as a green circle. The temperature reaches 160 °C after 8 minutes of sonication (red arrows).

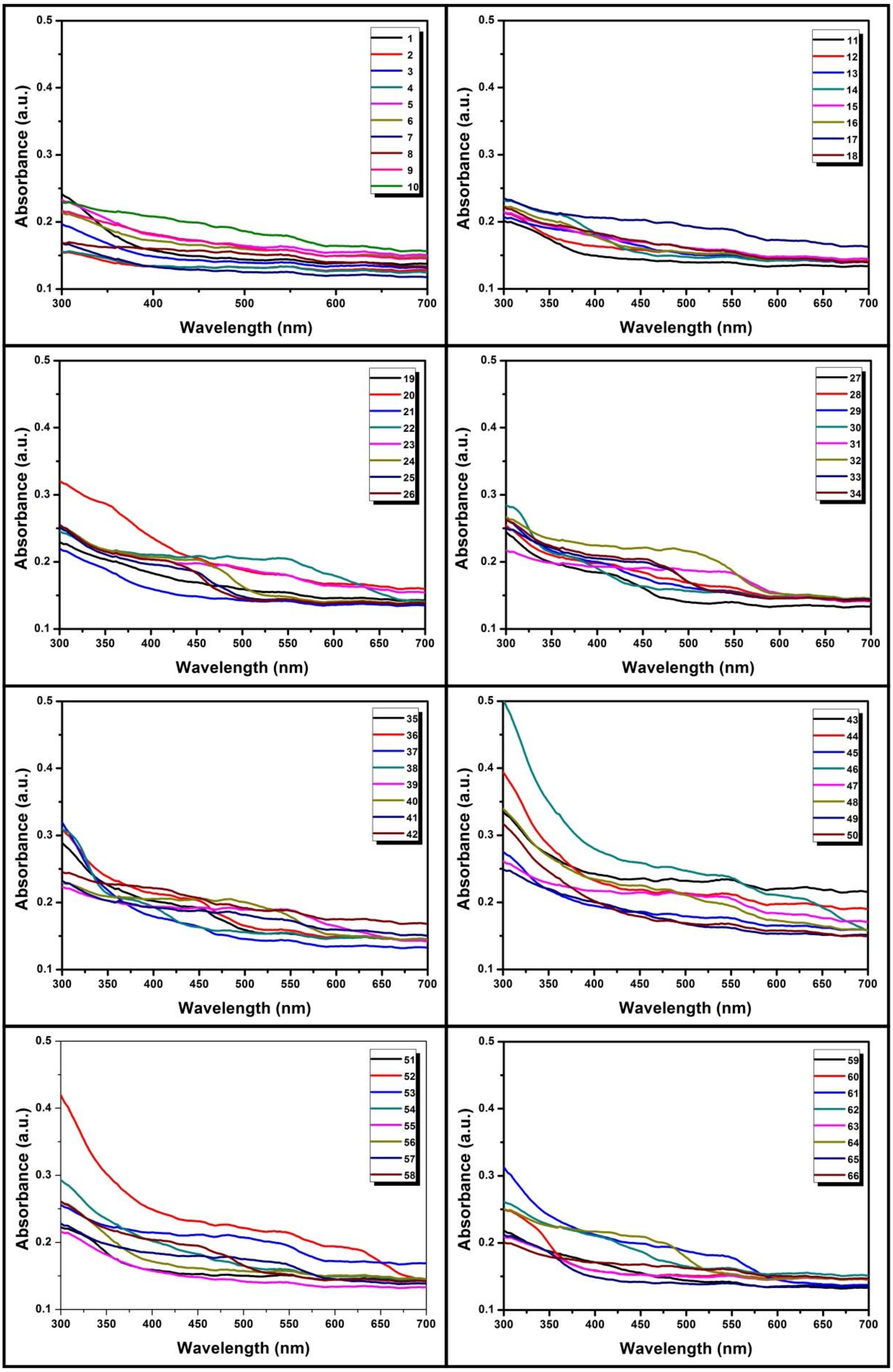

Fig. S3 UV-Visible absorption spectra of all $(Zn_xAg_yIn_z)S_2$ NCs.

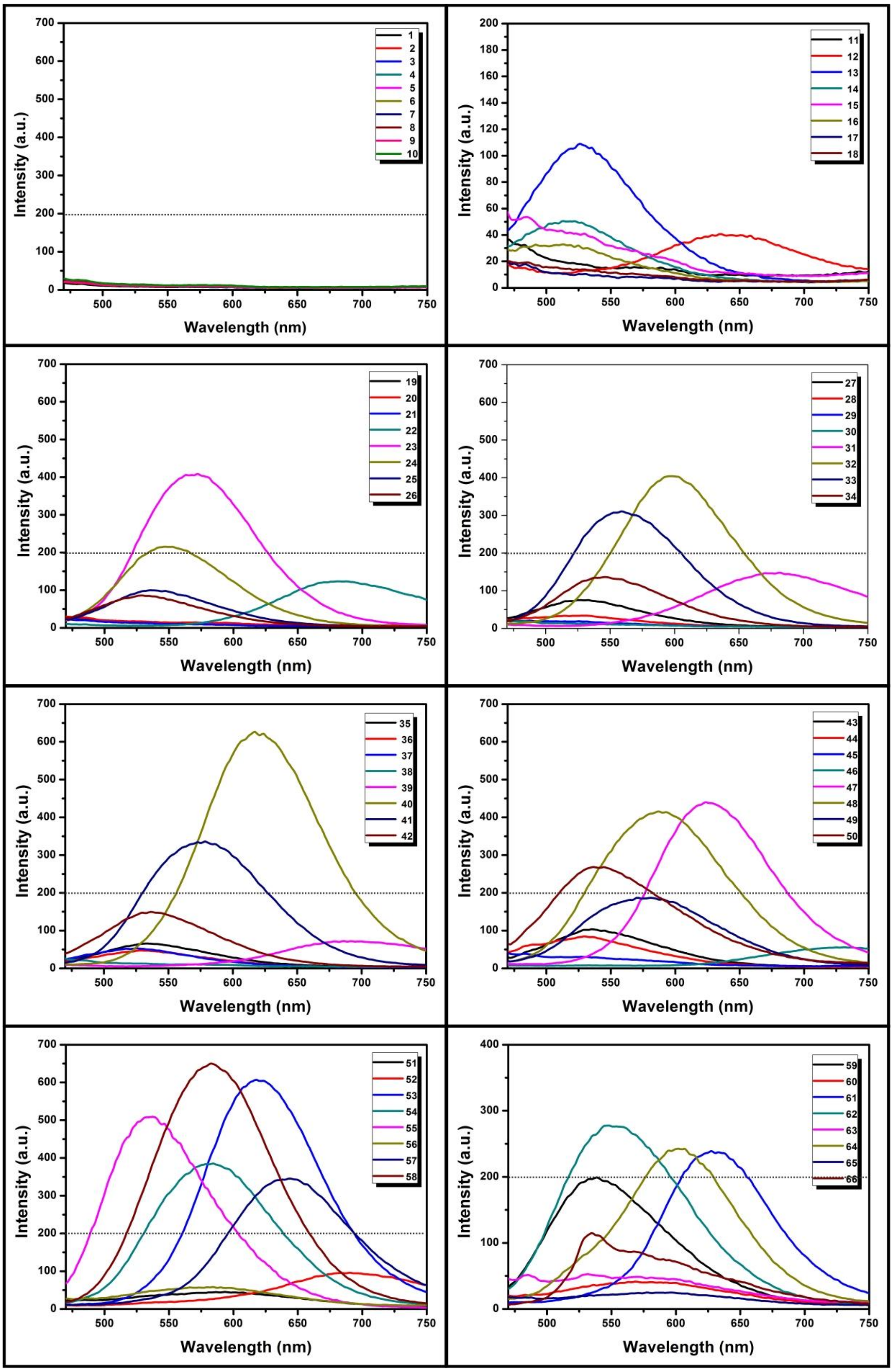

Fig. S4 Emission spectra of all $(Zn_xAg_yIn_z)S_2$ NCs by excitation at 365 nm.

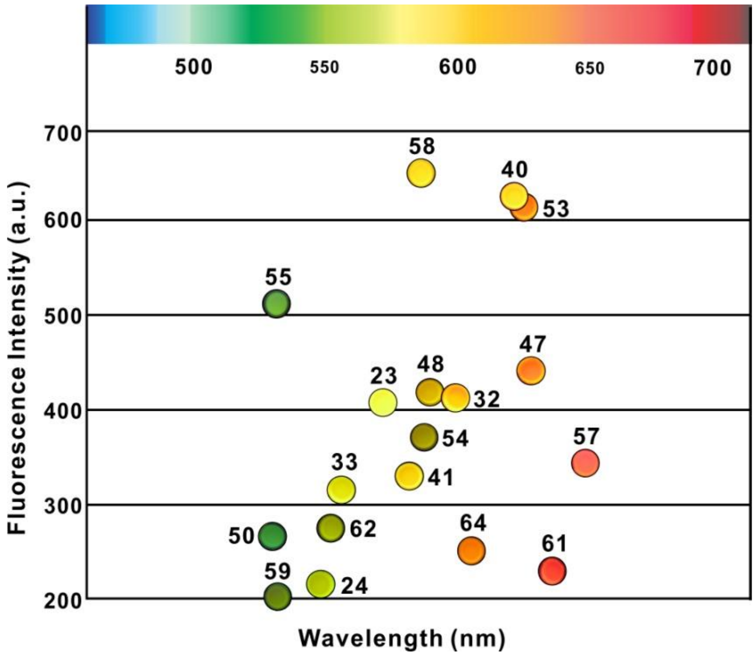

Fig. S5 Distribution of tZAIS NCs according to emission intensities and wavelengths.

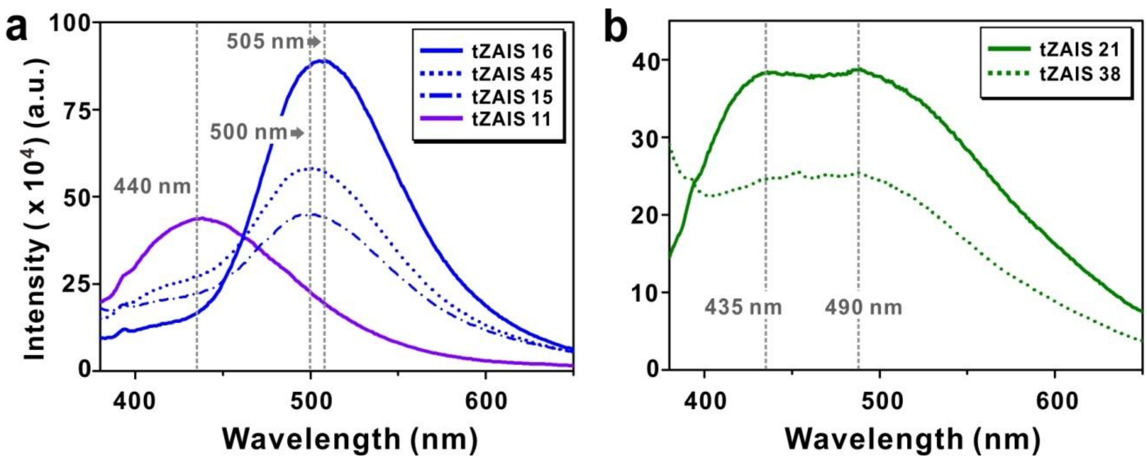

Fig. S6 tZAIS NCs with emission maxima at blue-shifted wavelength **(a)** and dual emission spectra **(b)**. Detail compositional information of blue-colored ZAIS NCs are as follows; $(Zn_1Ag_0In_0)S_2$ [tZAIS 11], $(Zn_{0.3}Ag_{0.6}In_{0.1})S_2$ [tZAIS 15], $(Zn_{0.4}Ag_{0.5}In_{0.1})S_2$ [tZAIS 16], $(Zn_{0.6}Ag_0In_{0.4})S_2$ [tZAIS 45]. ZAIS NCs with double or multiple emission maxima are $(Zn_{0.9}Ag_0In_{0.1})S_2$ [tZAIS 21], $(Zn_{0.7}$Ag0$In_{0.3})S_2$ [tZAIS 38].

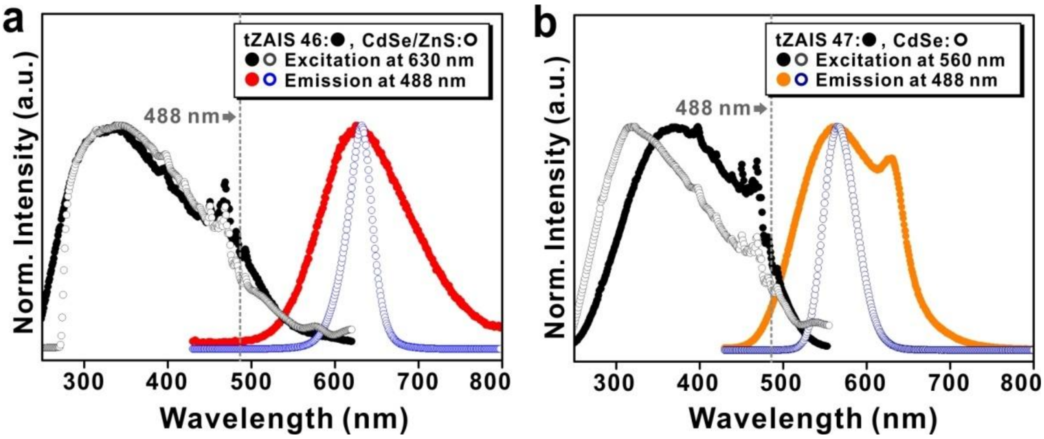

Fig. S7 Excitation and emission spectra of tZAIS 46 and CdSe/ZnS **(a)**, and tZAIS 47 and CdSe **(b)**. Closed circles represent spectra of ZAIS NC and open circles show QD's spectra (CdSe/ZnS and CdSe). Excitation wavelengths (Black/white circles) were scanned at a fixed emission wavelength either at 630 nm **(a)** or at 560 nm **(b).** All emission wavelength scans (the colored circles) were obtained at 488 nm excitation. All photoluminescence spectra were normalized.

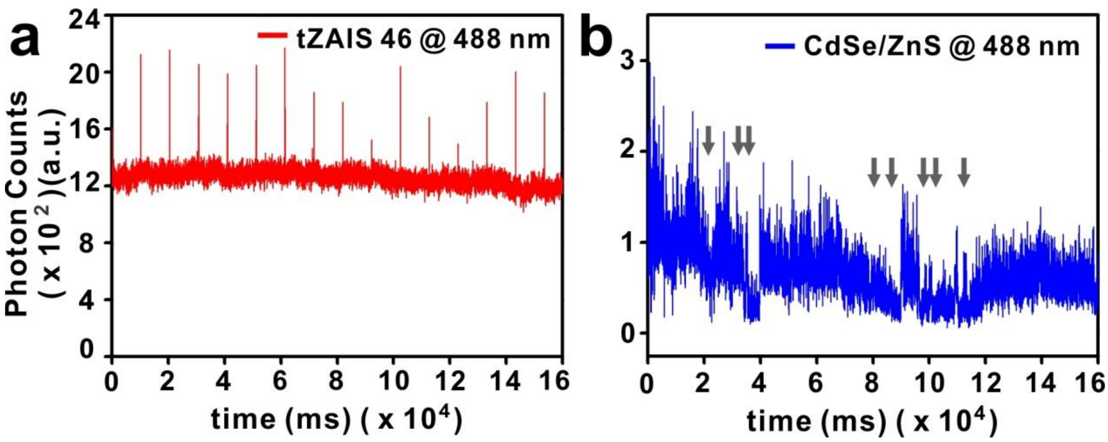

Fig. S8 Photon trajectories of single tZAIS 46 NC **(a)** and CdSe/ZnS QD **(b)**. Intensity of single tZAIS NC is 7 ~ 10 times brighter than CdSe/ZnS QD's case. Although there is significant blinking phenomena in CdSe/ZnS QD as previously reported[1,2], tZAIS NC doesn't show any noticeable blinking. Gray arrows represent a dark state of CdSe/ZnS QD which is converted from a bright state. Photon trajectories were collected by adjusting the Piezo stage to the position of single nanocrystal after a confocal scanning image was obtained.

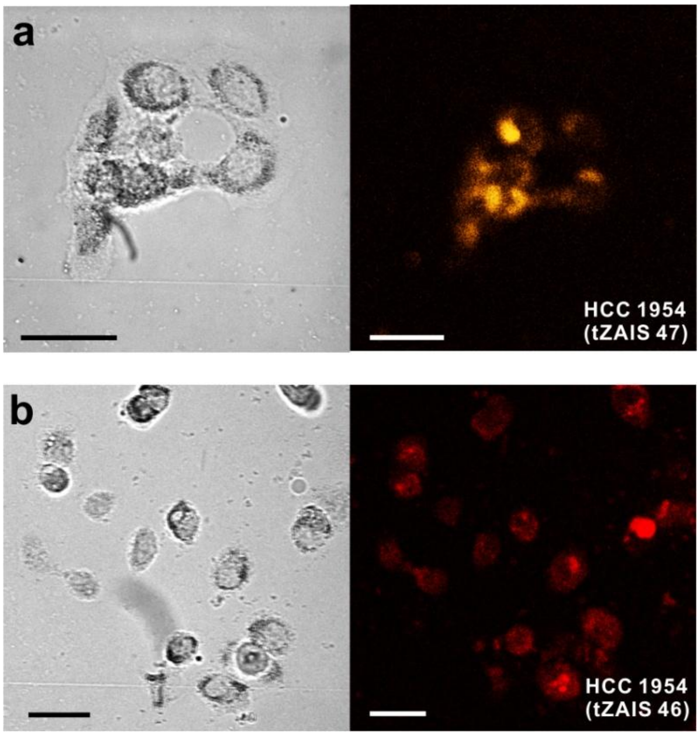

Fig. S9 Confocal fluorescence images of HCC 1954 cells containing tZAIS 47 NCs **(a)** and tZAIS 46 NCs **(b)**. Left panels show bright field images and right panels are confocal fluorescence images (scale bar is 50 μm).

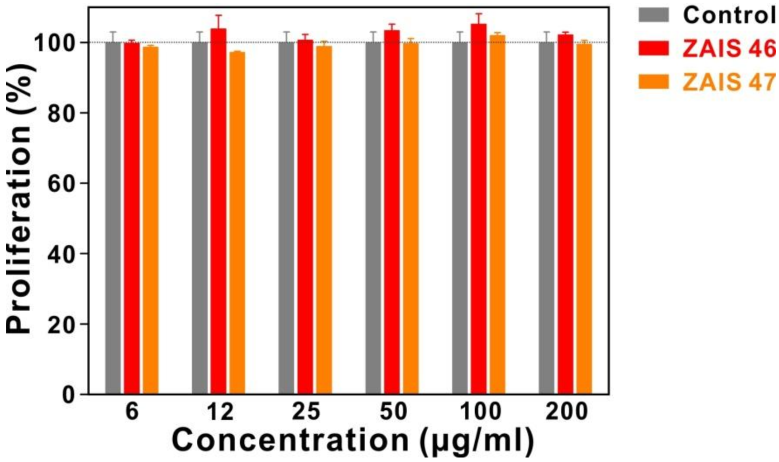

Fig. S10 MTT cell viability assay of breast cancer cells (MCF-7) in various concentration range of the $(Zn_xAg_yIn_z)S_2$ NCs. Cells are viable and there is no apparent cytotoxic effect up to 200 μg/ml of the NCs.

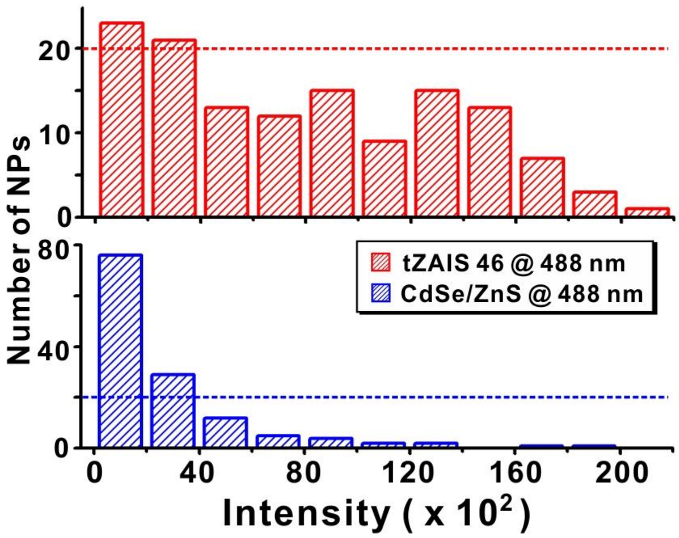

Fig. S11 Histogram of intensity distributions for single tZAIS 46 (top) and QD (bottom) at 488 nm excitation. Intensity of single NCs was calculated by multiplying mean intensity and defined area using ImageJ. The total numbers of analyzed particles were 135.

1. X. Wang, X. Ren, K. Kahen, M. A. Hahn, M. Rajeswaran, S. Maccagnano-Zacher, J. Silcox, G. E. Cragg, A. L. Efros, T. D. Krauss, *Nature* 2009, **459**, 686.

2. B. Mahler, P. Spinicelli, S. Buil, X. Quelin, J. P. Hermier, B. Dubertret, *Nat Mater* 2008, **7**, 659.